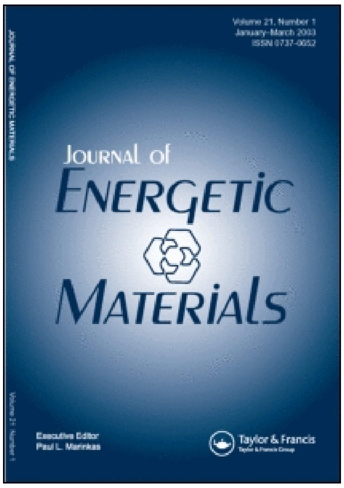

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Research towards novel energetic materials

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RESEARCH TOWARDS NOVEL ENERGETIC MATERIALS

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ABSTRACT

Compact, three-dimensional cage compounds containing optimum numbers of nitro groups as determined in theory by thermohydrodynamic calculations, constitute a class of explosive compounds more powerful than HMX. This is a direct result of high crystal densities, particularly in combination with high strain energies built into certain of the cage systems. The synthesis of polynitro cage compounds has progressed on several fronts, and is currently in the second stage of a three-stage effort. The first stage has seen the synthesis of forerunners of more highly nitrated cage compounds, as part of a broad strategy to develop the methodology

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for achieving the polynitration of cage molecules. The nitro cage compounds whose syntheses are in progress (second stage) and will be completed in the near future are expected to be energetic. These compounds, in turn, are expected to lead, in the third stage, to still more highly nitrated cage compounds including those which will be significantly more powerful than HMX. The results of the synthesis effort to date are outlined, and achievements highlighted. In addition, the results of the calculations identifying the optimum polynitro cage compounds are discussed. The future direction of the program of synthesis is indicated.

INTRODUCTION

This paper summarizes the current status of research directed towards the synthesis of a new class of energetic compounds, viz. the carbocyclic polynitro cage compounds. These are molecules with compact, closed, three-dimensional cage-type skeletal frames whose faces consist of rings of carbon atoms. The program of synthesis is based on the underlying principle that the detonation pressure of an explosive increases as the square of its density[1], coupled with the fact that three-dimensional cage molecules are inherently more dense than their open-structured molecular counterparts. The density of cubane*, for example, has been calculated from x-ray data as 1.288 g/cm^3, as compared to a density of only

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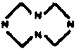
*The structure of cubane is depicted in Table 1.

Table 1. Properties of Carbocyclic Cage Compounds with Nitro Content Optimized for Maximum Detonation Output, as Calculated by the Kamlet-Jacobs Simple Method

Parent Hydrocarbon Cage Compound	Composition of Polynitro Cage C (no.)	H (no.)	NO_2 (no.)	ρ (g/cm3)	ΔH^o_f (kcal/mole)	Molecular Strain Energy (kcal/mole)	Ave. C-C Bond Strain Energy (kcal/mole)	P_{CJ} (kbar)
 Tetrahedrane	4	0	4	2.138	88.03	126	21.0	512
 Triprismane	6	0	6	2.138	80.03	137	15.2	493
 Cubane	8	0	8	2.098[a]	81.04	157	13.1	467
 Homocubane	9	1	9	2.094	30.08	122	9.4	453
 1,3-Bishomocubane	10	1	11	2.092	-33.83	82.6	5.9	431
 Bishomopentaprismane	12	2	12	2.057	-56.76	70.1	4.1	421
 Trishomocubane	11	2	12	2.063	-75.3	57.1	3.8	419
 Diamantane	14	5	15	2.048	-170.47	9.8	0.5	415
 Adamantane	10	5	11	1.959	-136.69	5.6	0.5	383
 HMX[b]	4[c]	8	4	1.903	17.4	0	0	382

[a] Modified by taking cubane as basis for calculation.
[b] Included for comparison.
[c] The two-dimensional ring contains four nitrogen atoms in addition.

0.93 for the isomeric $(CH)_8$ eight-membered, tub-shaped ring compound, cyclooctatetraene.

We deal here with a number of target compounds of the carbocyclic cage variety, which have been synthesized as part of a broad strategy to develop the methodology for achieving the polynitration of cage molecules, and whose syntheses constitute milestones on the way to optimum nitrated cage compounds (the parent hydrocarbon cages are depicted in Table 1). We discuss first theoretical calculations and their results which both support and expand the rationale for the synthesis of polynitro cage compounds. It will be seen that the calculations, which have identified the optimum polynitro cage compounds, predict detonation performance substantially higher than that of HMX, currently the best military explosive. The prediction stems from a combination of (i) high crystal densities which become even higher as the number of nitro groups increases, and (ii) high strain energies which can be built into the cages, increasing as more of the faces consist of smaller-size strained rings.

Most importantly, it is likely that some of the target cage compounds will not only have high "energy density," but also low sensitivity to initiation. That the polynitrocubanes will be thermally stable compounds is supported by calculations performed by J. Alster and M.J.S. Dewar, et al. (ARDEC and University of Texas) indicating that nitro substitution on cubane, which is comprised of four-membered rings and, therefore, under considerable structural strain, will not significantly alter its thermal stability[2,3]. Calculated heats of dissociation, moreover, have shown that any weakening of carbon-hydrogen and carbon-nitrogen bonds attributable to a nearby nitro substituent is insignificant[4]. Subsequent experimental observations on the thermal behavior of over twenty cage compounds lend credence to the favorable forecast regarding thermal stability[5]. The studies on thermal stability show also that, while cubane derivatives in general are thermally stable, bishomocubane and adamantane derivatives are even more stable in accordance with reduced cage strain in these molecules.

CALCULATION OF DETONATION PERFORMANCE

Thermohydrodynamic calculations were carried out to determine the theoretical number of nitro groups which, when attached to the carbocyclic cages, would yield the maximum detonation performance. The equations of the Kamlet-Jacobs Simple Method (KJSM)[1] were used to calculate the Chapman-Jouguet detonation pressures. This method for the most part yields results in reasonable agreement with those provided by the more highly complex TIGER computer code[6]. A significant advantage to its use is that insight into the important parameters that influence the detonation performance is gained more easily than with the TIGER code.

Both the KJSM and TIGER computations require an input of the density and heat of formation of the explosive, which includes the strain energy when strain is present in the molecule, as well as the elemental composition. Densities were calculated using the methods of Cady[7] and Stine[8], the former having a theoretical basis although incorporating an empirical packing fraction, the latter using an empirical calibrating base of over two thousand compounds. In those cases where the density of the parent cage compound or derivative is known, the methods are modified to correct for any small difference occurring between the calculated and observed densities, thus providing more accurate density values for the polynitro derivatives. Calculated densities were found to agree reasonably well with values obtained experimentally from nitro cage compounds synthesized subsequent to the calculations, confirming that the densities can be estimated with reasonable accuracy.

Heats of formation were estimated using the Arthur D. Little bond value method for calculating the heats of combustion for systems without strain[9], and strain energies were added to the estimated values as required for the strained cage systems. In those cases where strain energies were not available from the literature, they were estimated from the values known for simple ring compounds[10]. Although not as accurate as the estimations of density, the estimated heats of formation do not require high accuracy for the calculations of detonation pressure, since, according to the KJSM equations[1], the detonation pressure is a very weak function of the heat of formation of the explosive.

RESULTS OF CALCULATIONS FOR MAXIMIZING DETONATION PERFORMANCE OF POLYNITRO CAGE COMPOUNDS

It can be seen from the data summarized in Table 2 that for the nitrocubanes, as the number of nitro groups is increased, detonation pressures (P_{CJ}) increase as a result of both the improving oxygen balance and increasing densities (ρ). The detonation pressure is at a maximum when all eight hydrogen atoms in cubane are replaced, producing octanitrocubane which has maximum density and is oxygen-balanced. The effect of adding nitro groups to the cubane cage is typical for carbocyclic cages of the type, $(CH)_n$. The adamantane cage, on the other hand, consists of six CH_2 groups in addition to four CH's (see structure, Table 1), and the effect of adding nitro groups is quite different.

The data summarized in Table 3 for the nitroadamantanes show that the detonation pressure reaches a maximum at eleven nitro groups, and decreases as nitro groups continue to be added up to the maximum number of sixteen groups which, in theory, can be attached to the adamantane cage. As with cubane (Table 2), a steady (linear) increase in density and decrease in heat of formation occurs as the number of nitro groups increases. However, oxygen balance is attained at eleven nitro groups, and becomes

Table 2. Detonation Pressures of the Nitro Derivatives of Cubane, as Calculated by the Kamlet-Jacobs Simple Method

# of Nitro Groups	ρ (g/cm^3)	ΔH^o_f (kcal/mole)	P_{CJ} (kbar)
2	1.66	132	205
3	1.78	124	270
4	1.87	115	323
5	1.94	107	368
6	2.00	98	406
7	2.06	90	439
8	2.10	81	467

Table 3. Detonation Pressures of the Nitro Derivatives of Adamantane, as Calculated by the Kamlet-Jacobs Simple Method

# of Nitro Groups	ρ (g/cm^3)	ΔH^o_f (kcal/mole)	P_{CJ} (kbar)
4	1.584	-76.78	182
6	1.729	-93.90	253
8	1.838	-111.01	312
10	1.923	-128.13	361
11	1.959	-136.69	383
12	1.992	-145.25	381
13	2.022	-153.81	372
16	2.096	-179.49	342

increasingly positive as more groups are added. In the region of positive oxygen balance, therefore, the influence of density on the detonation pressure is less important than in the region of negative oxygen balance. Thus, from the standpoint of detonation performance, there is no advantage to be gained in synthesizing an adamantane containing more than eleven nitro groups. (Nevertheless, oxygen-positive adamantanes might serve as organic oxidizers.) The heats of formation of the nitroadamantanes are very negative, reflecting the relatively strain-free state of the adamantane cage; those of the nitrocubanes are positive, pointing to the strain residing in the cubane cage.

The data listed in Table 1 show the theoretical number of nitro groups required for maximum detonation performance of the illustrated carbocyclic cage structures. It can be seen that (i) the detonation pressures for the optimum polynitro cage compounds increase as the densities increase, while (ii) the densities increase as the number of small rings making up the skeletal cages increase. Molecular strain energies reach a maximum in octanitrocubane, then decrease in hexanitrotriprismane and tetranitrotetrahedrane despite higher average C-C bond strain energies. This is the result of triprismane and tetrahedrane being small cages with fewer bonds than cubane. That tetranitrotetrahedrane shows the highest detonation pressure is in accord with the fact that it possesses the highest average C-C bond strain energy. The calculations indicate that adamantane bearing eleven nitro groups is close to HMX in detonation output, while all the other polynitro cage compounds listed in Table 1 are significantly more powerful, with some exceeding HMX by as much as 20-35%.

APPROACHES TO THE SYNTHESIS OF POLYNITRO CAGE COMPOUNDS

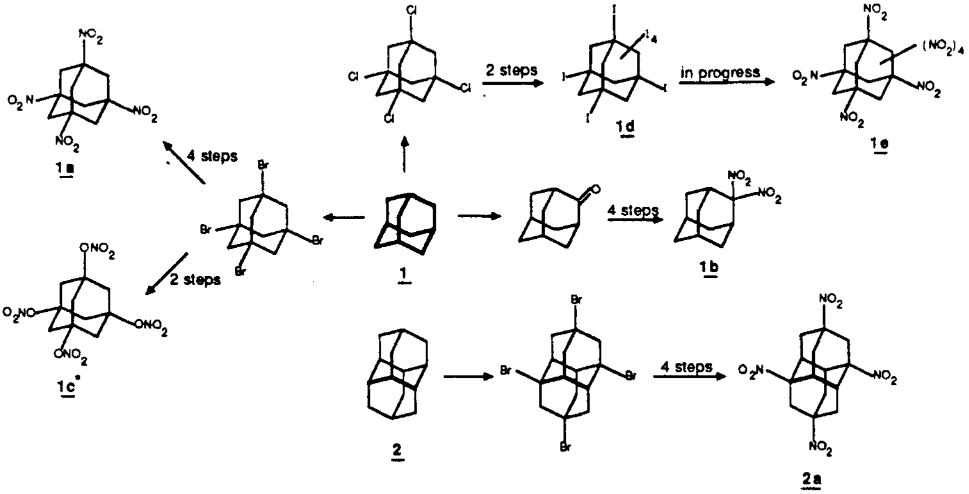
As discussed above, thermohydrodynamic calculations have identified the optimum polynitro cage compounds yielding maximum detonation performance for each of the hydrocarbon cage structures illustrated in Table 1. The optimum compounds thus constitute the ultimate targets in the synthesis of energetic materials more powerful than HMX. A number of nitro cage compounds which are viewed as intermediate targets or milestones en route to the ultimate compounds (Table 1) have now been prepared and are reported here. All are thermally stable substances. They are but forerunners of the more highly nitrated cage compounds whose synthesis the research, both in progress and planned, is designed to achieve.

From the outset of this program, it appeared likely that direct nitration of unsubstituted hydrocarbon cage compounds would not provide a useful synthetic route to polynitro cage compounds. Various attempts to nitrate adamantane directly, for example, have reportedly produced mono- and dinitroadamantanes, and even trinitroadamantane, but at elevated temperature and pressure, and only in very low yield[11]. Indirect approaches were adopted instead for the synthesis of the target compounds, consisting of (i) polysubstitution of a hydrocarbon cage, and subsequent conversion of the substituents to nitro groups (Fig. 1); (ii) synthesis (construction) of a polysubstituted hydrocarbon cage from appropriately functionalized precursors, and subsequent transformation of the substituents to nitro groups (Fig. 2). Other more direct approaches are actively being investigated, since they may prove to be viable synthetic routes to certain of the target compounds. These investigations were started only recently, however, and are therefore not addressed in this paper. Consistent with the effort to develop, in an orderly manner, the chemical strategies necessary to achieve the synthesis of the ultimate targets, the number of nitro groups introduced into a cage system is being increased in a gradual and orderly fashion, thereby permitting stepwise evaluation of the effect of increasing nitro substitution on stability and explosive properties.

INDIRECT APPROACHES

The earliest example of this type of approach was the synthesis of 1,3,5,7-tetranitroadamantane (1a), the first cage compound containing four nitro groups[11]. This was accomplished at ARDEC starting with readily available adamantane (1), and progressing stepwise by way of tetrabromination, exchange with iodine, replacement with amide groups, hydrolysis to amino groups, and oxidation to the nitro groups. 1,4,6,9-Tetranitrodiamantane (2a),

Figure 1. Polynitro Cage Compounds via Functionalization of Hydrocarbon Cages



*The nitro groups in 1c are bonded to the cage through oxygen, producing the tetranitrate.

Figure 2. Polynitro Cage Compounds via Construction of Appropriately Substituted Hydrocarbon Cages

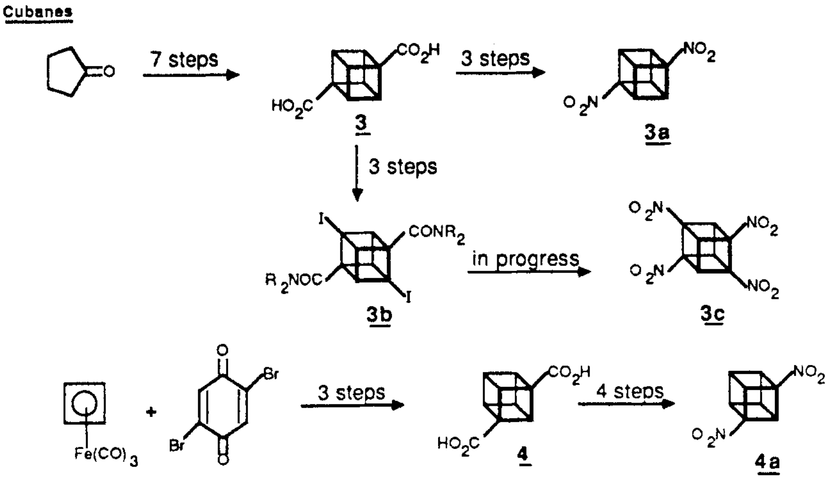
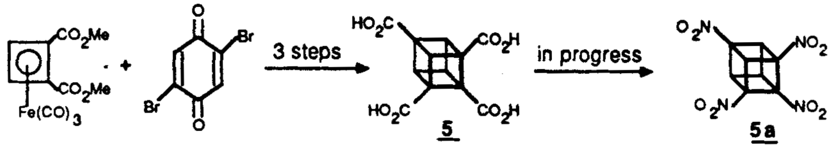
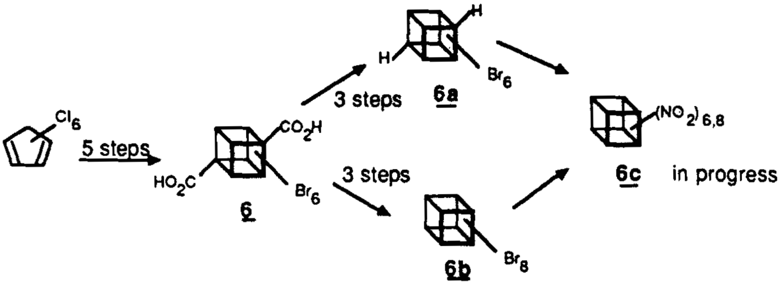


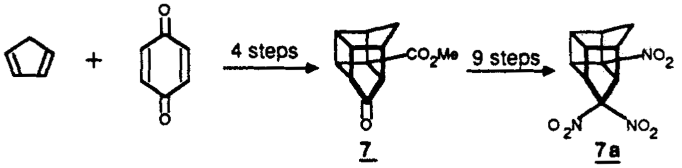
Figure 2, continued

Cubanes, continued





Bishomocubanes



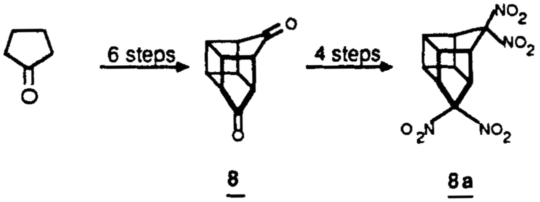
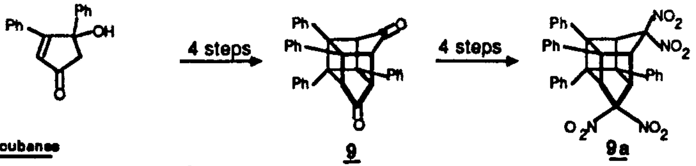
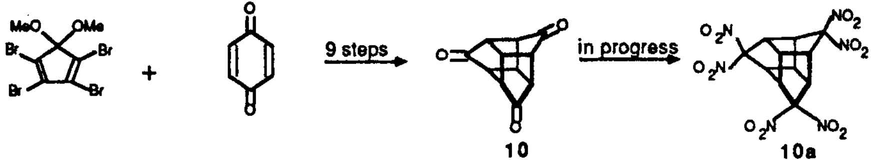


Figure 2, continued

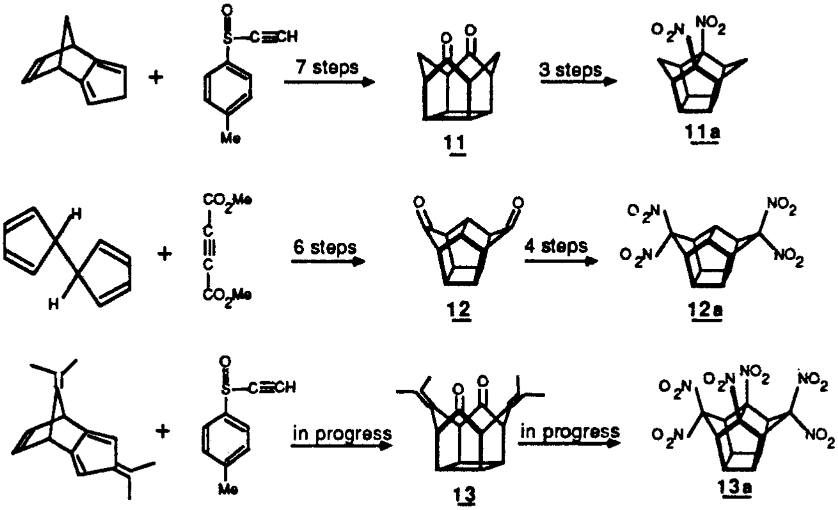
Bishomocubanes, continued



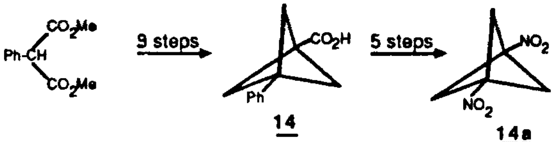
Trishomocubanes



Bishomopentaprismanes



Bicyclopentanes



the second cage compound to contain four nitro groups, was also synthesized at ARDEC by a similar reaction sequence[12] starting with diamantane (2).

2,2-Dinitroadamantane (1b), prepared at ARDEC as the forerunner of related tetra- and hexanitroadamantanes, was obtained via adamantanone and oxime formation followed by a three-step transformation through gem-bromonitro to gem-dinitro[13]. Still another type of derivative synthesized at ARDEC was the 1,3,5,7-tetranitrate of adamantane (1c) obtained via bromination and formation of the tetrahydroxy compound[14].

More recently, as a result of an ARDEC finding that polychlorinated adamantanes can be converted to their iodinated counterparts by halogen exchange, octachloroadamantane was converted to the octaiodo compound (1d)[15], a near precursor of octanitroadamantane (1e). The octachloro derivative was obtained from Professor P.v.R. Schleyer and his group (University of Erlangen-Nurnberg) who synthesized it from adamantane by photochlorination of the thermally prepared tetrachloro intermediate. Octanitroadamantane (1e) is only three nitro groups short of the optimum number predicted by the theoretical calculations (Table 1), and an effort to produce 1e using the same methodology cited above for tetranitroadamantane (1a) is currently in progress at ARDEC. Practical syntheses for both adamantane and diamantane were pioneered much earlier by Prof. Schleyer at Princeton University[16].

Professor P.E. Eaton (University of Chicago) succeeded in preparing 1,4-dinitrocubane (3a) from the dicarboxycubane (3) in three steps involving carbamate formation, hydrochlorinolysis to the diamine, and oxidation to the nitro groups[17]. His synthesis of the dicarboxycubane, reported much earlier[18], started with cyclopentanone and proceeded, in seven steps, through ethylene ketal formation and bromination, generation of the bromo diene and dimerization, cage closing with ketal hydrolyses, and finally, ring contractions producing the disubstituted cubane.

Professor G.W. Griffin (University of New Orleans) later prepared 1,4-dinitrocubane (3a) from the dicarboxycubane (3) in four steps, in a variation of the Eaton procedure (above), generating the acid chloride and isocyanate prior to the diamine. He then synthesized 1,3-dinitrocubane (4a) starting with cyclobutadiene irontricarbonyl and 2,5-dibromobenzoquinone, generating 1,3-dicarboxycubane (4) in three steps by addition, cage closing and ring contractions. The conversion of 4 to 4a was accomplished using the same procedure as for transforming 3 to 3a[19].

The diiododiamidocubane 3b (R = iPr) was obtained by Professor Eaton using the diisopropylamide group to promote lithium-induced "ortho"-mercuration of the cubane frame. This was an important breakthrough in that the first direct functionalization of a highly strained cage system had been achieved. Higher degrees of iodination have already been accomplished, and the synthesis of a tetranitrocubane, viz. 3c, now appears to be achievable in the near future. The probability of success is heightened by the recent extension of the synthesis of 4 to that of 1,2,3,5-tetracarboxycubane (5), precursor of tetranitrocubane 5a, at ARDEC by a former research associate of Prof. Griffin[20].

Other polysubstituted cubanes recently synthesized, and which are potentially useful as intermediates en route to the more highly nitro-substituted cubanes, include hexabromocubane-1,4-dicarboxylic acid (6), prepared by Prof. Griffin who achieved ring contraction of the octabrominated cage precursor. The latter had already been prepared[21] starting with hexachlorocyclopentadiene in a four-step procedure resembling the original synthesis of 3 [18]. The fully substituted cubane (6) was decarboxylated to produce hexa- and octabromocubanes, possible precursors of the polynitrocubanes 6c, by replacement with hydrogen and bromine, respectively (6a and 6b). In view of the newness and highly challenging nature of the chemistry of cubane and other strained cage molecules, the above achievements in polysubstitution represent important breakthroughs in the field. Efforts to transform cubanes 6a and 6b as well as 3b and 5 to the nitro derivatives are in progress.

Professor A.P. Marchand (North Texas State University), focusing on the 1,3-bishomocubane system, prepared the 3,5,5-trinitro derivative (7a) in thirteen steps starting with cyclopentadiene and p-benzoquinone via generation of the appropriately substituted cage system 7. The final product (7a) was obtained from the oxime by stepwise conversion to gem-dinitro, and subsequent transformation of carbomethoxy to nitro by way of carbamate and amine formation[22]. Trinitro derivative 7a is an important "first" from the standpoint that nitration of both secondary and tertiary carbons has been achieved in the same molecule, opening the door to higher nitration in the bishomocubane and other systems. The synthesis of 5,5,9,9-tetranitrobishomocubane (8a) was accomplished in a ten-step procedure closely paralleling the synthesis of 3, starting with cyclopentanone, but in this case generating the diene devoid of bromine to obtain the cage dione 8. Mono- then gem-dinitro groups were introduced into 8 by way of dioxime formation[23].

Similarly, the tetraphenyl cage dione 9 was generated in four steps from the appropriate phenyl-substituted cyclopentenone, and converted in four more steps to the tetranitrobishomocubane 9a with four phenyl groups attached. The latter can be transformed, in principle, to nitro groups to generate the octanitrobishomocubane. Most recently the synthesis of trishomocubane trione 10 was achieved by Prof. Marchand in a series of nine steps from the ketal of tetrabromocyclopentadiene and p-benzoquinone[24]. An effort to introduce six nitro groups into 10 to produce the hexanitrotrishomocubane 10a is currently in progress.

Professor L.A. Paquette (Ohio State University), concentrating on the bishomopentaprismane system, has prepared both dinitro (11a) and tetranitro (12a) derivatives[25]. The former, which is the first known vicinal dinitro cage compound, was synthesized in ten steps from a tricyclodecatriene and p-toluenesulfonylacetylene via formation of the [4]-peristylane dione 11. The nitro groups were then introduced by way of the dioxime, and debromination of the bis-bromonitro derivative completed the cage structure. Dinitro derivative 11a, with nitro groups on adjacent carbons, has special significance in that, in fully nitrated cage systems, all (adjacent) carbons are substituted with nitro groups. Tetranitro derivative 12a was next prepared in ten steps starting with 9,10-dihydrofulvalene and an acetylenedicarboxylate, proceeding to the bishomopentaprismane dione 12, and introducing the nitro groups via dioxime formation. The synthesis of the hexanitro derivative 13a, starting with p-toluenesulfonylacetylene and the appropriate tricyclodecatriene to generate the [4]-peristylane dione 13, is currently being pursued.

An extension of the KJSM calculations (cf. Table 1) to bicyclopentane, another strained polycyclic system offering high energy-density capability, has optimized the nitro content at six groups for achieving maximum detonation output (P_{CJ}, 411 kbar; ave. C-C strain energy, 13.5 kcal/mole; density, 1.991 g/cm^3; ΔH_f^0, 5.27). In pursuit of this target compound, Professor K.B.

Wiberg (Yale University) has recently synthesized 1,3-dinitrobicyclopentane (14a) starting with dimethyl phenylmalonate in fourteen steps generating the phenylbicyclopentanecarboxylic acid (14) as intermediate[26]. The preparation of the 2,2-dinitro compound via the 2-ketone is currently in progress.

SUMMARY AND CONCLUSIONS

Compact, three-dimensional cage compounds containing optimum numbers of nitro groups as determined in theory by thermohydrodynamic calculations, constitute a class of energetic materials more powerful than HMX. This is a direct result of high crystal densities, particularly in combination with high strain energies built into certain of the cage systems. Nitro groups have been introduced into seven varieties of carbocyclic cage compounds, including, in descending order of molecular strain and density, cubane, bishomocubane, bishomopentaprismane, and adamantane. Twelve thermally stable derivatives containing as many as four nitro groups have been synthesized to date, serving as forerunners of more highly nitrated cage compounds which are expected to be energetic. The syntheses of eight such potentially energetic compounds, with four to eight nitro groups, are in progress at the present time, and appear to be achievable in the near future. These compounds, in turn, are expected to lead to still more highly nitrated cage compounds nearly all of which, according to the theoretical calculations, will be significantly more powerful than HMX, exceeding its detonation output in some cases by as much as 20-35%. Both calculations and experiment predict that nitro substitution will not significantly alter the thermal stability of the hydrocarbon cage molecules, and that some of the ultimate target compounds should not only have high "energy density" but also low sensitivity to initiation.

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